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Addition of boranes to iminophosphines: Synthesis and reactivity of a new bulky hydroboration reagent

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ABSTRACT

Two sterically diverse iminophosphines have been prepared from the addition of 2-$Ph_2PC(O)H$ and 4-$H_2NC_6H_4OMe$ (**L1**) and 2,6-$H_2NC_6H_4(i\text{-}Pr)_2$ (**L2**), and the addition of boranes to these substrates has been examined in an effort to reduce the imine C=N bond. Reactions using borane-dimethylsulfide with the smaller imine **L1** afforded adducts arising from initial coordination to the phosphorus atom and then the imine nitrogen. Addition of excess borane-dimethylsulfide eventually led to reduction of the imine and generated an active H_2BNRR' unit, which went on to make several aminophosphine products. The sterically hindered imine **L2** was used to retard the reactivity in the resulting aminoborane. Hydroboration studies with a new borane (**7**) showed good selectivity in reactions with 1-octene and vinyl arenes. Reactions of iminophosphines with alkyl and dialkylborane also gave adducts, making reduction of the imine increasingly difficult. Addition of the dialkoxyboranes, catecholborane and pinacolborane, were promising for the less hindered imine, but harsh reaction conditions (metal catalysts, microwave reactor and elevated temperatures and pressures) were required in reductions of the sterically-hindered imine, giving rise to complicated product distributions.

1. Introduction

Amines are a remarkably important class of compounds that have widespread applications in industry and are key intermediates in many organic transformations [1]. A common and efficient method of generating substituted amines is via the reductive amination of aldehydes or ketones, which generally proceeds by initial condensation with a primary or secondary amine to give a carbinolamine intermediate and subsequently dehydrates to afford the imine or iminium ion (Scheme 1). Reduction of the imine then generates the substituted amine, where the choice of reducing agent is critical to the success of the reaction. Although catalytic hydrogenation is usually an effective way of reducing simple imines, these additions can sometimes give mixtures of products. For instance, with substrates containing both an alkene and an imine functionality, competing reduction of both unsaturated groups often results in low yields of the desired product. Another limitation to this method involves reducing substrates containing divalent sulfur, which may inhibit and eventually deactivate the catalyst system. An alternate and selective method for generating amines from imines invokes the use of hydride reducing agents, especially boron hydrides such as $NaBH_4$. Although a plethora of borohydride derivatives have subsequently been designed for this purpose, reactions can suffer from low yields and poor selectivities [2–6], especially in the case of sterically-hindered imine substrates, as well as toxic side products, as observed in cases utilizing $NaBH_3CN$. As a result, a considerable amount of research has concentrated on the development of less toxic and more selective boron hydride reagents for these important reactions.

Our interest in studying the addition of B–H bonds to unsaturated organic molecules, naturally lead us to the reduction of imines. In this study we have investigated the addition of electronically- and sterically-diverse boranes to iminophosphines derived from the addition of aniline derivatives to 2-diphenylphosphinobenzaldehyde. There has been recent considerable interest in the use of unsymmetrical bidentate ligands containing both a nitrogen (amine) and phosphorus donor atom, referred to as (P,N)-ligands, for their potential applications in coordination chemistry and in homogenous catalysis [7–11]. Ligands of this sort are of interest as they provide transition metals with a 'hard' amine and 'soft' phosphine donor, allowing them to stabilize a variety of oxidation states and induce attractive transformations.

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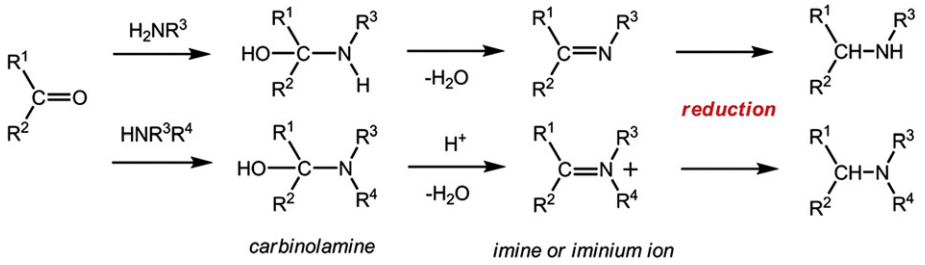


Scheme 1. General reductive amination pathways.

2. Experimental

2.1. General methods

Reagents and solvents were purchased from Aldrich Chemicals and used as received. Rh(acac)(dppb) [12], dimesitylborane [13], and **L1** and **L2** [14] were synthesized by previously reported methods. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR (^{1}H 270 MHz; ^{11}B 87 MHz; ^{13}C 68 MHz; and ^{31}P 109 MHz) spectrometer. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^{1}H and ^{13}C) or external $BF_3{\cdot}OEt_2$ (^{11}B) or H_3PO_4 (^{31}P)] and coupling constants (J) in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), septet (sept), multiplet (m), broad (br), and overlapping (ov). Microwave reactions were performed using a CEM Discover SP system in standard closed vessels with the reaction temperature monitored by the internal IR pyrometer. GC–MS analyses were conducted using a Varian Saturn 2000 MS, coupled to a CP-3800 GC. The GC was equipped with the 1177 injection port with a CP-8410 liquid autoinjector connected to an SPB-1 (Supelco) fused-silica column (30 m × 0.25 mm i.d. × 0.25 μm) attached to a 50 cm transfer line. Elemental analyses were performed by Guelph Chemical Laboratories (Guelph, ON). All reactions were performed under an atmosphere of nitrogen.

2.2. Synthesis and reactivity

2.2.1. Synthesis of *1*

To a stirred toluene (5 mL) solution of **L1** (395 mg, 1.00 mmol) was added a toluene solution of $H_3B{\cdot}SMe_2$ (0.5 mL of a 2.0 M solution, 1.0 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum. The resulting yellow solid was dissolved in hot Et_2O (8 mL) and the solution stored at −30 °C. After 3 days, a precipitate was collected by suction filtration to afford **1** as a yellow solid. Yield: 260 mg (64%). Spectroscopic NMR data (in $CDCl_3$): ^{1}H δ: 8.83 (s, 1H, C(*H*)=N), 8.40 (ddd, J_{HH} = 7.6, 3.7, 1.0 Hz, 1H, Ar), 7.72–7.34 (ov m, 12H, Ar), 7.05 (dd, J_{HH} = 12.1, 7.6 Hz, 1H, Ar), 6.77 (m, 4H, Ar), 3.76 (s, 3H, OC*H*$_3$), 1.66 (br s, 3H, B*H*$_3$); ^{11}B δ: −36 (br); ^{13}C{^{1}H} δ: 158.6, 156.2 (d, J_{CP} = 6.7 Hz), 144.0, 139.7 (d, J_{CP} = 7.7 Hz), 134.1 (d, J_{CP} = 7.2 Hz), 133.5 (d, J_{CP} = 9.2 Hz), 131.7, 131.6, 130.3 (d, J_{CP} = 9.7 Hz), 129.5 (d, J_{CP} = 8.2 Hz), 129.2 (d, J_{CP} = 9.7 Hz), 128.7, 128.4 (d, J_{CP} = 7.7 Hz), 122.7, 114.2, 55.5; ^{31}P{^{1}H} δ: 20.6. Anal. calcd for $C_{26}H_{25}NBOP$ (409.33): C 76.29, H 6.17, N 3.42; found: C 76.03, H 5.99, N 3.15.

2.2.2. Synthesis of *2*

To a stirred toluene (5 mL) solution of **L1** (395 mg, 1.00 mmol) was added a toluene solution of $H_3B{\cdot}SMe_2$ (1.0 mL of a 2.0 M solution, 2.0 mmol). The reaction was allowed to proceed for 18 h at which point the solvent was removed under vacuum to afford a yellow solid. The solid was dissolved in Et_2O (10 mL) and the solution stored at −30 °C. After several days a yellow precipitate was collected by suction filtration to afford **2**. Yield: 160 mg (38%). Spectroscopic NMR data (in $CDCl_3$): ^{1}H δ: 8.87 (s, 1H, C(*H*)=N), 8.23 (dd, J_{HH} = 7.6, 3.7 Hz, 1H, Ar), 7.74–7.44 (ov m, 12H, Ar), 7.05 (dd, J_{HH} = 12.1, 7.6 Hz, 1H, Ar), 6.77 (m, 4H, Ar), 3.77 (s, 3H, OC*H*$_3$), 2.11 (br s, 3H, B*H*$_3$), 1.51 (br s, 3H, B*H*$_3$); ^{11}B δ: −15 (br), −38 (br); ^{13}C{^{1}H} δ: 166.1 (d, J_{CP} = 5.1 Hz), 159.6, 144.2, 144.1 (d, J_{CP} = 8.7 Hz), 133.7 (d, J_{CP} = 9.7 Hz), 133.5 (d, J_{CP} = 9.2 Hz), 133.1 (d, J_{CP} = 8.2 Hz), 132.2, 131.7, 130.4, 129.4 (d, J_{CP} = 10.2 Hz), 129.2 (d, J_{CP} = 8.2 Hz), 128.3, 123.4, 113.9, 55.6; ^{31}P{^{1}H} δ: 21.1. Anal. calcd for $C_{26}H_{28}NB_2OP$ (423.17): C 73.79, H 6.68, N 3.31; found: C 74.11, H 6.42, N 3.09.

2.2.3. Reaction of *L1* with 4 equivalents of $H_3B{\cdot}SMe_2$

To a stirred toluene (5 mL) solution of **L1** (100 mg, 0.25 mmol) was added a toluene solution of $H_3B{\cdot}SMe_2$ (0.5 mL of a 2.0 M solution, 1.0 mmol). The reaction was allowed to proceed for 18 h at which point the solvent was removed under vacuum and the reaction analyzed by multinuclear NMR spectroscopy. Selected spectroscopic NMR data (in $CDCl_3$): ^{1}H δ: 8.89 (s, C(*H*)=N), 8.74 (s, C(*H*)=N), 8.23 (dd, J_{HH} = 7.7, 3.7 Hz, Ar), 7.92–7.36 (ov m, Ar), 7.24–7.04 (ov m, Ar), 6.95–6.28 (ov m, Ar), 4.98 (s), 4.73 (m), 4.65 (s), 3.77 (s, OC*H*$_3$), 3.72 (s, OC*H*$_3$), 3.69 (s, OC*H*$_3$), 3.62 (s, OC*H*$_3$), 1.77 (br s, B*H*$_3$), 1.36 (br s, B*H*$_3$); ^{11}B δ: 42 (br), −15 (br), −38 (br); ^{31}P{^{1}H} δ: 22.2, 19.8.

2.2.4. Synthesis of *3*

To a stirred toluene (5 mL) solution of **L1** (800 mg, 2.02 mmol) was added a toluene (2 mL) solution of catecholborane (250 mg, 2.08 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum. The resulting pale yellow oil was triturated with Et_2O (3 × 1 mL) to afford **3** as a white solid. Yield: 911 mg (88%). Spectroscopic NMR data (in $CDCl_3$): ^{1}H δ: 7.44–7.23 (ov m, 13H, Ar), 7.15–7.05 (ov m, 4H, Ar), 7.20–6.96 (ov m, 2H, Ar), 6.87 (m, 1H, Ar), 6.76 (d, J_{HH} = 8.9 Hz, 2H, Ar), 5.08 (d, J_{HP} = 2.2 Hz, 2H, C*H*$_2$), 3.76 (s, 3H, OC*H*$_3$); ^{11}B δ: 26 (br); ^{13}C{^{1}H} δ: 155.9, 148.7, 142.9 (d, J_{CP} = 22.0 Hz), 137.0, 136.1 (d, J_{CP} = 10.2 Hz), 135.2 (d, J_{CP} = 14.8 Hz), 134.1 (d, J_{CP} = 19.5 Hz), 133.5, 129.1, 128.9 (d, J_{CP} = 18.9 Hz), 128.8, 127.2, 127.0 (d, J_{CP} = 4.6 Hz), 123.9, 122.0, 114.2, 111.8, 55.5, 50.3 (d, J_{CP} = 27.1 Hz); ^{31}P{^{1}H} δ: −15.5. Anal. calcd for $C_{32}H_{27}NBO_3P$ (515.41): C 74.57, H 5.29, N 2.72; found: C 74.32, H 5.12, N 2.88.

2.2.5. Synthesis of *4*

To a stirred MeOH (5 mL) suspension of Rh(acac)(dppb) (400 mg, 0.64 mmol) was added a MeOH (5 mL) solution of **3** (328 mg, 0.64 mmol). The reaction mixture was allowed to proceed for 18 h at which point the clear red solution was concentrated to 3 mL under vacuum. Upon standing for 18 h at RT an orange precipitate formed and was collected by suction filtration to afford **4**. Yield: 249 mg (34%). Spectroscopic NMR data (in THF-d_8): ^{1}H δ: 7.58–7.05 (ov m, 29H, Ar), 6.94–6.71 (ov m, 6H, Ar), 6.64 (d, J_{HH} = 8.4 Hz, 2H, Ar), 6.48 (t, J_{HH} = 8.2 Hz, 1H, Ar), 6.28–6.18 (ov m, 8H, Ar), 4.69 (br s, 1H, C*H*HNH), 4.11 (br s, 1H, CH*H*NH), 3.76 (s, 3H, OC*H*$_3$), 3.48 (t, J_{HH} = 11.0 Hz, 1H, CH$_2$N*H*), 2.30 (br m, 2H, C*H*$_2$), 2.19 (br m, 2H, C*H*$_2$), 1.95 (br m, 2H, C*H*$_2$), 1.59 (br m, 2H, C*H*$_2$); ^{11}B δ: 14.4

(sharp); $^{13}C\{^1H\}$ δ: 158.6, 153.1, 140.5 (m), 139.3 (d, J_{CP} = 14.5 Hz), 137.5, 136.7 (d, J_{CP} = 4.2 Hz), 136.1, 134.2 (m), 134.0, 133.0 (m), 132.2, 130.7, 130.5 (m), 129.6, 128.8 (m), 128.4, 128.0, 125.1, 122.2, 116.2, 114.0, 107.3, 58.2 (d, J_{CP} = 15.1 Hz), 55.1, 27.6 (d, J_{CP} = 21.8 Hz), 26.2 (d, J_{CP} = 27.5 Hz), 23.3, 20.6; $^{31}P\{^1H\}$ δ: 45.6 (ddd, J_{PRh} = 160 Hz, J_{PP} = 51, 37 Hz), 25.6 (ddd, J_{PP} = 291 Hz, J_{PRh} = 160 Hz, J_{PP} = 37 Hz), 10.5 (ddd, J_{PP} = 291 Hz, J_{PRh} = 155 Hz, J_{PP} = 50 Hz). Anal. calcd for $C_{66}H_{60}NBO_5P_3Rh$ (1153.98): C 68.69, H 5.25, N 1.21; found: C 69.32, H 5.45, N 1.31.

*2.2.6. Synthesis of **5***

To a stirred THF (2 mL) solution of **L1** (300 mg, 0.76 mmol) and Rh(acac)(dppb) (10 mg, 0.02 mmol) was added a THF (2 mL) solution of pinacolborane (100 mg, 0.78 mmol). The reaction mixture was heated in a CEM microwave reactor at 125 °C for 0.5 h. Removal of solvent under vacuum afforded a yellow oil which was dissolved in hot hexane (2 mL) and the solution stored at −30 °C. After 3 days a pale yellow precipitate was collected by suction filtration to afford **5**. Yield: 286 mg (72%). Spectroscopic NMR data (in $CDCl_3$): ^1H δ: 7.67 (m, 1H, Ar), 7.37–7.28 (ov m, 6H, Ar), 7.12–7.01 (ov m, 8H, Ar), 6.89 (t, J = 7.4 Hz, 1H, Ar), 6.70 (d, J_{HH} = 8.2 Hz, 2H, Ar), 5.26 (s, 2H, CH_2), 3.26 (s, 3H, OCH_3), 1.06 (s, 12H, pin); ^{11}B δ: 24 (br); $^{13}C\{^1H\}$ δ: 154.9, 144.5 (d, J_{CP} = 21.5 Hz), 139.4, 136.5 (d, J_{CP} = 10.7 Hz), 135.1 (d, J_{CP} = 15.4 Hz), 134.3 (d, J_{CP} = 19.5 Hz), 133.2, 129.0, 128.7 (d, J_{CP} = 6.7 Hz), 128.1, 126.8, 126.2 (d, J_{CP} = 5.1 Hz), 122.0, 114.0, 82.6, 54.6, 50.0 (d, J_{CP} = 28.2 Hz), 24.4; $^{31}P\{^1H\}$ δ: −15.1. Anal. calcd for $C_{32}H_{35}NBO_3P$ (523.49): C 73.41, H 6.75, N 2.68; found: C 73.66, H 7.02, N 2.33.

*2.2.7. Synthesis of **6***

To a stirred toluene (5 mL) solution of **L2** (450 mg, 1.00 mmol) was added a toluene solution of $H_3B{\cdot}SMe_2$ (0.5 mL of a 2.0 M solution, 1.0 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum. The resulting solid was dissolved in hot Et_2O (3 mL) and the solution stored at −30 °C. A yellow precipitate was collected by suction filtration to afford **6** as a bright yellow solid. Yield: 357 mg (77%). Spectroscopic NMR data (in $CDCl_3$): ^1H δ: 8.66 (s, 1H, C(H)═N), 8.62 (ddd, J_{HH} = 7.9, 3.9, 1.2 Hz, 1H, Ar), 7.67–7.38 (ov m, 12H, Ar), 7.07–7.01 (ov m, 4H, Ar), 2.61 (sept, J_{HH} = 6.8 Hz, 2H, $CH(CH_3)_2$), 1.56 (br s, 3H, BH_3), 0.96 (d, J_{HH} = 6.8 Hz, 12H, $CH(CH_3)_2$); ^{11}B δ: −36 (br); $^{13}C\{^1H\}$ δ: 159.2 (d, J_{CP} = 6.7 Hz), 148.6, 139.1 (d, J_{CP} = 8.2 Hz), 137.0, 134.3 (d, J_{CP} = 6.1 Hz), 133.4 (d, J_{CP} = 9.2 Hz), 131.7, 130.8 (d, J_{CP} = 9.2 Hz), 130.0, 129.5, 129.2 (d, J_{CP} = 9.7 Hz), 128.7, 128.6 (d, J_{CP} = 8.2 Hz), 124.1, 122.7, 27.8, 23.2; $^{31}P\{^1H\}$ δ: 20.8. Anal. calcd for $C_{31}H_{35}NBP$ (463.48): C 80.33, H 7.63, N 3.02; found: C 80.12, H 7.82, N 3.16.

*2.2.8. Reaction of **L2** with 2 equivalents of $Me_2S{\cdot}BH_3$*

To a stirred toluene (5 mL) solution of **L2** (360 mg, 0.80 mmol) was added a toluene solution of $H_3B{\cdot}SMe_2$ (0.8 mL of a 2.0 M solution, 1.6 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum and the reaction analyzed by multinuclear NMR spectroscopy. Selected spectroscopic NMR data (in $CDCl_3$): ^1H δ: 9.35 (s, C(H)═N), 9.20 (s, C(H)═N), 8.70 (m, Ar), 7.78–7.39 (ov m, Ar), 7.24–6.96 (ov m, Ar), 6.81 (m, Ar), 4.61 (s, CH_2), 2.67 (sept, J_{HH} = 6.6 Hz, $CH(CH_3)_2$), 2.48 (sept, J_{HH} = 6.6 Hz, $CH(CH_3)_2$), 2.16 (br s, BH_3), 1.19 (d, J_{HH} = 6.6 Hz, $CH(CH_3)_2$), 1.17 (d, J_{HH} = 6.6 Hz, $CH(CH_3)_2$), 0.85 (d, J_{HH} = 6.6 Hz, $CH(CH_3)_2$), 0.75 (d, J_{HH} = 6.6 Hz, $CH(CH_3)_2$); ^{11}B δ: 42 (br), −14 (br), −37 (br); $^{31}P\{^1H\}$ δ: 23.8, 22.6, 21.2.

*2.2.9. Synthesis of **7***

To a stirred toluene (5 mL) solution of **L2** (450 mg, 1.00 mmol) was added a toluene solution of $H_3B{\cdot}SMe_2$ (1.5 mL of a 2.0 M solution, 3.0 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum. The resulting solid was dissolved in hot Et_2O (5 mL) and the solution stored at −30 °C. A precipitate was collected by suction filtration to afford **7** as a white solid. Yield: 391 mg (82%). Spectroscopic NMR data (in $CDCl_3$): ^1H δ: 7.62–7.33 (ov m, 12H, Ar), 7.22–7.12 (ov m, 2H, Ar), 7.01–6.98 (ov m, 2H, Ar), 6.89 (ddd, J_{HH} = 11.9, 7.9, 1.2 Hz, 1H, Ar), 4.62 (s, 2H, CH_2), 4.37 (br s, 2H, NBH_2), 2.86 (sept, J_{HH} = 6.8 Hz, 2H, $CH(CH_3)_2$), 1.51 (br s, 3H, BH_3), 0.97 (d, J_{HH} = 6.8 Hz, 6H, $CH(CH_3)_2$), 0.91 (d, J_{HH} = 6.8 Hz, 6H, $CH(CH_3)_2$); ^{11}B δ: 39 (br), −37 (br); $^{13}C\{^1H\}$ δ: 145.0, 144.3, 142.8 (d, J_{CP} = 10.7 Hz), 134.5 (d, J_{CP} = 7.2 Hz), 133.3 (d, J_{CP} = 9.7 Hz), 131.4, 131.1, 129.6, 128.9 (d, J_{CP} = 10.2 Hz), 128.8, 128.0, 127.5 (d, J_{CP} = 8.7 Hz), 127.0, 123.8, 59.6 (d, J_{CP} = 5.6 Hz), 27.9, 25.1, 23.4; $^{31}P\{^1H\}$ δ: 21.2. Anal. calcd for $C_{31}H_{38}NB_2P$ (477.32): C 78.00, H 8.04, N 2.94; found: C 77.74, H 7.76, N 2.90.

*2.2.10. Reaction of **L2** with catecholborane*

To a stirred THF (1 mL) solution of **L2** (200 mg, 0.44 mmol) was added a THF (1 mL) solution of catecholborane (53 mg, 0.44 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum to give an orange-colored oil which was analyzed by multinuclear NMR spectroscopy. Selected spectroscopic NMR data (in $CDCl_3$): ^1H δ: 8.17 (m, Ar), 7.55–6.86 (ov m, Ar), 5.70 (d, J_{HH} = 12.1 Hz), 4.91 (d, J_{HP} = 2.2 Hz), 3.91 (sept, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 3.11 (sept, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 2.83 (sept, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.54 (d, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.30 (d, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.07 (d, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.03 (d, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 0.84 (d, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 0.18 (d, J_{HH} = 6.8 Hz, $CH(CH_3)_2$); ^{11}B δ: 22 (br); $^{31}P\{^1H\}$ δ: −16.2, −17.3.

*2.2.11. Synthesis of **11***

To a stirred THF (2 mL) solution of **L2** (300 mg, 0.67 mmol) and Rh(acac)(dppb) (3 mg, 0.005 mmol) was added a THF (2 mL) solution of pinacolborane (171 mg, 1.34 mmol). The reaction mixture was heated in a CEM microwave reactor at 125 °C for 0.5 h. Removal of solvent under vacuum gave an orange oil which was dissolved in hot hexane (2 mL) and stored at −30 °C. A pale orange solid precipitated after several days and was collected by suction filtration to afford **11**. Yield: 94 mg (24%). Spectroscopic NMR data (in $CDCl_3$): ^1H δ: 7.45 (m, 1H, Ar), 7.29–7.22 (ov m, 9H, Ar), 7.12–6.96 (ov m, 6H, Ar), 6.78 (m, 1H, Ar), 4.64 (d, J_{HP} = 2.7 Hz, 2H, CH_2), 3.11 (sept, J_{HH} = 6.9 Hz, 2H, $CH(CH_3)_2$), 1.29 (s, 12H, pin), 1.11 (d, J_{HH} = 6.9 Hz, 6H, $CH(CH_3)_2$), 0.80 (d, J_{HH} = 6.9 Hz, 6H, $CH(CH_3)_2$); ^{11}B δ: 20 (br); $^{13}C\{^1H\}$ δ: 147.3, 144.6 (d, J_{CP} = 27.0 Hz), 138.9, 137.6 (d, J_{CP} = 13.0 Hz), 136.6 (d, J_{CP} = 14.5 Hz), 133.7 (d, J_{CP} = 20.2 Hz), 133.6, 131.3 (d, J_{CP} = 4.7 Hz), 128.8, 128.4 (d, J_{CP} = 6.5 Hz), 128.1, 127.3, 126.7, 123.5, 82.8, 52.0 (d, J_{CP} = 23.4 Hz), 27.0, 25.6, 24.7, 23.1; $^{31}P\{^1H\}$ δ: −16.6. Anal. calcd for $C_{37}H_{45}NBO_2P$ (577.64): C 76.93, H 7.87, N 2.43; found: C 77.14, H 8.22, N 2.64.

2.3. General method for hydroboration reactions

To a stirred C_6D_6 (0.5 mL) solution of **7** (89 mg, 0.19 mmol) was added a C_6D_6 (0.5 mL) solution of the appropriate substrate (0.19 mmol). The reaction mixture was heated at reflux for 4 h at which point the reaction was analyzed by multinuclear NMR spectroscopy. Products were confirmed by GC–MS following a basic, oxidative workup [14].

*2.3.1. Hydroboration of 1-octene with **7***

Spectroscopic NMR data (in C_6D_6): ^1H δ: 7.57 (m, Ar), 7.11–6.85 (ov m, Ar), 6.75 (t, J_{HH} = 7.6 Hz, Ar), 4.91 (s, NCH_2), 4.70 (br s, BH), 2.98 (sept, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 2.10 (br s, BH_3), 1.45 (br m, BCH_2), 1.32–1.18 (ov m, $-CH_2-$), 0.98 (d, J_{HH} = 6.8 Hz, $CH(CH_3)_2$),

0.89 (d, J_{HH} = 6.8 Hz, CH(CH_3)$_2$), 0.87 (t, J_{HH} = 6.6 Hz, CH_3); ^{11}B δ: 38 (br), −37 (br); ^{31}P{^{1}H} δ: 22.7.

2.3.2. Hydroboration of 4-vinylanisole with **7**

Selected spectroscopic NMR data (in C_6D_6): ^{1}H δ: 7.62 (m, Ar), 7.30 (m, Ar), 7.20–6.93 (ov m, Ar), 6.84 (d, J_{HH} = 8.6 Hz, Ar), 4.96 (s, CH_2), 4.77 (s, CH_2), 4.65 (br s), 3.37 (s, OCH_3), 3.36 (s, OCH_3), 3.35 (s, OCH_3), 3.03 (sept, J_{HH} = 6.9 Hz, $CH(CH_3)_2$), 2.89 (q, J_{HH} = 7.4 Hz, CH(B)CH_3), 2.65 (t, J_{HH} = 7.9 Hz, CH_2CH_2B), 2.10 (br s, BH_3), 1.53 (t, J_{HH} = 7.9 Hz, CH_2CH_2B), 1.24 (d, J_{HH} = 7.4 Hz, CH(B)CH_3), 1.08 (d, J_{HH} = 6.9 Hz, CH(CH_3)$_2$), 1.02 (d, J_{HH} = 6.9 Hz, CH(CH_3)$_2$), 1.01 (d, J_{HH} = 6.9 Hz, CH(CH_3)$_2$), 0.93 (d, J_{HH} = 6.9 Hz, CH(CH_3)$_2$); ^{11}B δ: 39 (br), 29 (br), −36 (br); ^{31}P{^{1}H} δ: 22.1, −16.6.

2.3.3. Hydroboration of 4-fluorostyrene with **7**

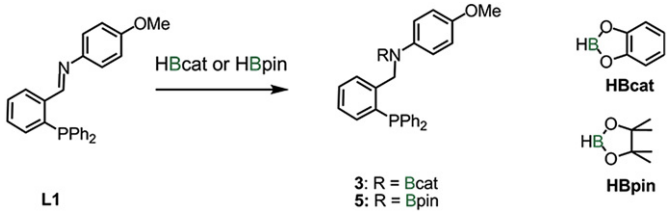
Selected spectroscopic NMR data (in C_6D_6): ^{1}H δ: 7.56 (m, Ar), 7.25 (m, Ar), 7.10–6.55 (ov m, Ar), 6.84 (d, J_{HH} = 8.6 Hz, Ar), 4.90 (s, CH_2), 4.73 (s, CH_2), 4.56 (br s), 3.25 (sept, J_{HH} = 6.9 Hz, $CH(CH_3)_2$), 2.97 (q, J_{HH} = 7.2 Hz, CH(B)CH_3), 2.41 (t, J_{HH} = 7.9 Hz, CH_2CH_2B), 2.04 (br s, BH_3), 1.30 (t, J_{HH} = 7.9 Hz, CH_2CH_2B), 1.08–0.98 (ov m), 0.97–0.94 (ov m), 0.89–0.86 (ov m); ^{11}B δ: 39 (br), 30 (br), −36 (br); ^{31}P{^{1}H} δ: 22.8, −16.4.

2.4. X-ray crystallography

Crystals of **3** and **4** were grown from saturated diethyl ether solutions at 25 °C. Crystals of **7** were grown from a saturated THF solution stored at −30 °C. Single crystals were coated with Paratone-*N* oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 10 s (**3** and **7**) and 30 s (**4**) exposure times. The detector distance was 5 cm. The data were reduced [15] and corrected for absorption [16]. The structures were solved by direct methods and refined by full-matrix least squares on F^2 [17]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were found in Fourier difference maps and refined using isotropic displacement parameters.

3. Results and discussion

The reduction of iminophosphines is a practical and efficient method of generating a wide variety of aminophosphine compounds. In this study, we initially investigated reductions of the sterically-accessible iminophosphine **L1** with a number of different boron hydride reagents. We have found that addition of one equivalent of $H_3B{\cdot}SMe_2$ at room temperature gave the phosphine borane adduct **1** as the only new boron-containing product (Scheme 2). The ^{11}B NMR spectrum for **1** shows a broad peak at δ −36 ppm for the coordinated borane along with a broad peak at δ 21 ppm in the ^{31}P NMR spectrum. Addition of a second equivalent of borane lead to moderate yields (*ca.* 35%) of the bis-adduct species



Scheme 3. Addition of boranes to iminophosphine **L1**.

2, along with a number of other products where the imine functionality has been. Addition of excess borane afforded a mixture of products where the imine double bond has been reduced and newly generated RR′NBH_2 species has either further reduced the starting material and/or adducts **1** and **2**. Addition of borane to isolated **2** once again lead to a mixture of products.

We then decided to look at other boron hydrides in an effort to affect this reduction more effectively by reducing the excessive amount of borane required to facilitate this reaction. Unfortunately, attempts to use thexylborane [18], 9-borabicyclo[3.3.1]-nonane [19] and dimesitylborane [12] gave numerous boron-containing products, as observed by ^{11}B NMR spectroscopy, presumably arising once again from competing coordination of these alkyl and dialkylboranes to the Lewis basic P and N atoms. Not surprisingly, reduction of the imine double bond became increasingly problematic with the increased size of the borane adducts.

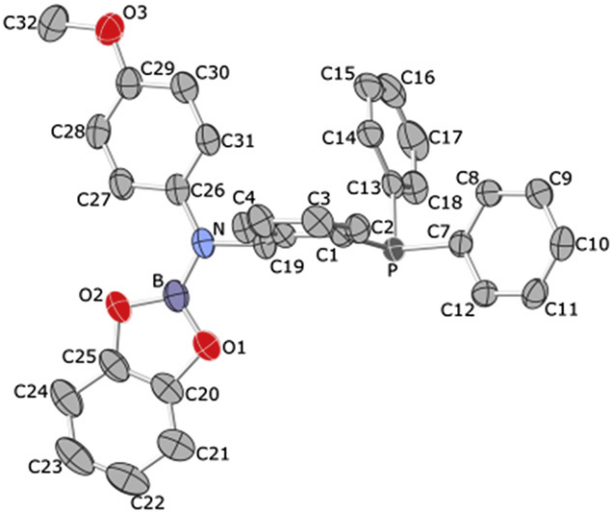
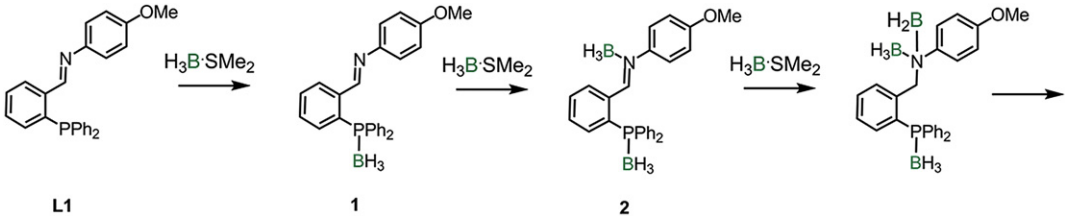


Fig. 1. The molecular structure of **3** with ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond distances (Å): P–C(7) 1.8329(17), P–C(13) 1.8350(18), P–C(1) 1.8431(16), C(19)–N 1.472(2), N–B 1.410(3), B–O(2) 1.399(2), B–O(1) 1.400(3). Selected bond angles (°): B–N–C(26) 126.85(15), B–N–C(19) 116.03(15), C(26)–N–C(19) 117.08(14), O(2)–B–O(1) 111.39(16), O(2)–B–N 127.91(18), O(1)–B–N 120.70(16).

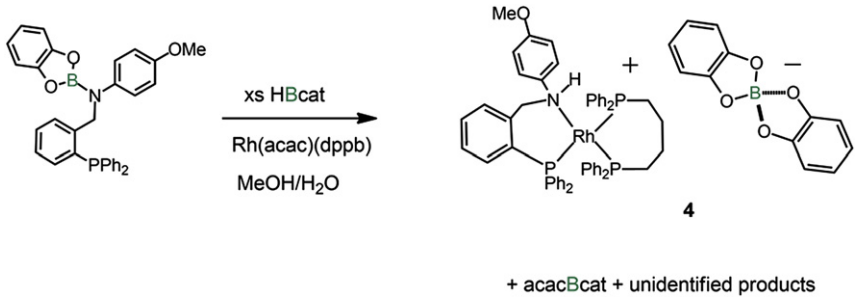


Scheme 2. Addition of borane-dimethylsulfide to iminophosphine **L1**.

Table 1
Crystallographic data-collection parameters.

Complex	**3**	**4**	**7**
Formula	$C_{32}H_{27}BNO_3P$	$C_{70}H_{67}BNO_6P_3Rh$	$C_{31}H_{38}B_2NP$
Molecular weight	515.33	1224.88	477.21
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/*n*	P-1	P2(1)/*c*
a/Å	10.8594(16)	12.311(6)	12.4812(8)
b/Å	13.6857(19)	14.083(6)	9.2948(6)
c/Å	17.851(3)	18.736(8)	24.2540(16)
α/°	90	77.990(6)	90
β/°	90.127(2)	73.175(6)	95.9980(10)
γ/°	90	77.456(7)	90
V/Å^3	2653.0(7)	2998(2)	2798.3(3)
Z	4	2	4
$\rho_{calc.}$/Mg m^{-3}	1.290	1.357	1.133
Crystal size/mm^3	0.40 × 0.30 × 0.20	0.20 × 0.20 × 0.05	0.65 × 0.40 × 0.20
Temp/K	198(1)	173(1)	198(1)
Radiation	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)
μ/mm^{-1}	0.138	0.419	0.118
Total reflections	18,157	20,707	18,914
Total unique reflections	5942	12,988	6247
No. of variables	451	740	468
θ Range/°	1.87–27.49	1.50–27.50	1.64–27.50
Largest difference peak/hole/*e* Å^{-3}	0.273 and −0.233	0.870 and −0.612	0.468 and −0.245
S (GoF) on F^2	1.061	1.020	1.054
*R*1[a] ($I > 2\sigma(I)$)	0.0380	0.0385	0.0397
w*R*2[b] (All data)	0.1011	0.1024	0.1143

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0339\cdot P)^2 + (0.7218\cdot P)]$ (**3**), $1/[\sigma^2(F_o^2) + (0.048\cdot P)^2 + (0.2178\cdot P)]$ (**4**), $1/[\sigma^2(F_o^2) + (0.0549\cdot P)^2 + (1.0288\cdot P)]$ (**7**), where $P = (\max(F_o^2, 0) + 2\cdot F_c^2)/3$.



Scheme 4. Generation of rhodium complex **4** from addition of HBcat to **3**.

Dialkoxyboron compounds are a considerably less Lewis acidic source of boron hydrides [20] and were examined next in an effort to avoid unwanted coordination with the Lewis basic phosphine and imine fragments (Scheme 3). As hoped, addition of catecholborane (HBcat, cat = 1,2-$O_2C_6H_4$) proceeded smoothly at room temperature over 18 h to give **3** as the major product along with a minor amount of decomposition product B_2cat_3 [21]. The ^{11}B NMR spectrum for **3** shows a broad peak at δ 26 ppm for the aminoborane along with a broad peak at δ −15.5 ppm in the ^{31}P NMR spectrum for the uncoordinated phosphorus atom (*c.f.* δ −14.3 ppm for the starting iminophosphine **L1**). The disappearance of the imine N=CH bond in the ^1H NMR spectra is followed by the appearance of a doublet at δ 5.08 ppm (J_{HP} = 2.2 Hz) corresponding to the reduced NCH_2 group in **3**. A similar disappearance for the imine carbon is observed in the ^{13}C NMR spectra along with the formation of a peak at δ 50.3 (d, J_{CP} = 27.1 Hz) ppm, observed for the reduced NCH_2 group. Compound **3** was also characterized by a single crystal X-ray diffraction study to confirm that the imine functionality was indeed reduced. The molecular structure of **3** is shown in Fig. 1 and crystallographic data provided in Table 1. The carbon–nitrogen bond is now reduced with a distance of C(19)–N 1.472(2) Å, and the aminoboron bond is N–B 1.410(3) Å, both of which are consistent with analogous compounds reported previously [22]. The boron oxygen bonds of B–O(2) 1.399(2) and B–O(1) 1.400(3) Å are typical for Bcat fragments. As expected, the chelating boron oxygen angles (O(2)–B–O(1) 111.39(16)°) are considerably shorter than the BN angles at O(2)–B–N 127.91(18)° and O(1)–B–N 120.70(16)°. There are no considerable P–B interactions in the solid state.

As relatively long reaction times (12–18 h) were required to facilitate the addition of HBcat to **L1**, we then decided to investigate the possibility of using a transition metal catalyst to accelerate this reaction. The transition metal catalyzed hydroboration of alkenes and alkynes is an important reaction in organic synthesis and considerable research has been conducted in this area [23]. Although a wide range of rhodium complexes can be used to catalyze this reaction, we have examined two of the most active and selective precatalysts in this study and found that catalytic amounts of $RhCl(PPh_3)_3$ could indeed be used to facilitate this addition, with only negligible amounts of decomposition products.

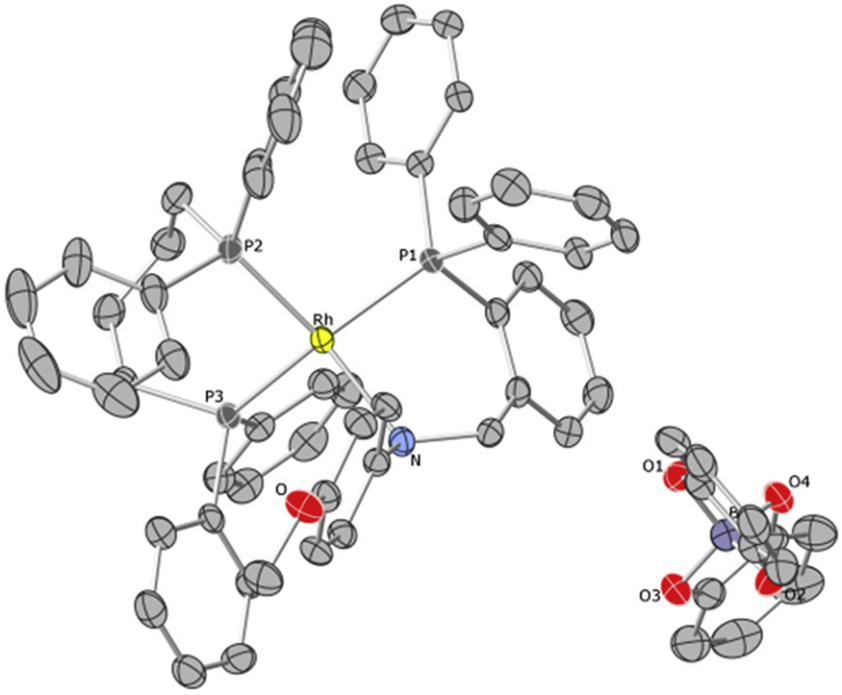
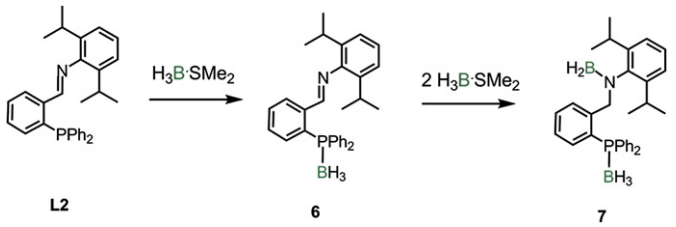


Fig. 2. The molecular structure of **4** with ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond distances (Å): Rh–N 2.205(2), Rh–P(2) 2.2356(9), Rh–P(1) 2.2894(9), Rh–P(3) 2.3393(10), B–O(1) 1.479(4), B–O(4) 1.479(4), B–O(3) 1.483(4), B–O(2) 1.493(4). Selected bond angles (°): N–Rh–P(2) 159.66(6), N–Rh–P(1) 88.45(6), P(2)–Rh–P(1) 99.95(4), N–Rh–P(3) 92.19(6), P(2)–Rh–P(3) 90.57(4), P(1)–Rh–P(3) 147.32(3), O(1)–B–O(4) 111.8(2), O(1)–B–O(3) 113.4(2), O(4)–B–O(3) 104.5(2), O(1)–B–O(2) 105.0(2), O(4)–B–O(2) 111.0(2), O(3)–B–O(2) 111.4(2), C(20)–N–Rh 96.86(14), C(19)–N–Rh 121.62(14), C(20)–N–C(19) 110.03(19).



Scheme 5. Addition of borane-dimethylsulfide to iminophosphine **L2**.

Reactions could also be catalyzed using 2–5 mol% of Rh(acac)(dppb) (acac = acetylacetonato, dppb = 1,4-bis(diphenylphosphino)-butane). This rhodium complex is a remarkably active and selective catalyst precursor for the hydroboration of a wide range of vinyl arenes using HBcat [11]. The active catalyst is believe to be derived from the zwitterionic species Rh(η^6-catBcat)(dppb), which arises from a boron-redistribution reaction during catalysis [11]. In this study, we have found that small amounts of [Rh(κ^2-*o*-$Ph_2PC_6H_4CH_2NHAr$)(dppb)][$Bcat_2$] (**4**, Ar = 4-C_6H_4OMe) crystallized out of solution upon completion of reactions using Rh(acac)(dppb). We hypothesized that compound **4** arises from the addition of the reduced product **3** with excess HBcat and adventitious water. Indeed, we were able to generate **4** in reactions of **3** with Rh(acac)(dppb) and excess HBcat in methanol, along with a number of redistribution and degradation products (Scheme 4). Once again, the formation of the $[Bcat_2]^-$ anion arises from a redistribution reaction. The ^{11}B NMR spectrum for **4** shows the expected sharp singlet at *ca.* δ 14 ppm, which is diagnostic for the $[Bcat_2]^-$ anion [11], and the ^{31}P NMR spectrum shows that all the phosphorus atoms in **4** are magnetically inequivalent. As such, each peak appears as a doublet of doublet of doublets, with coupling to rhodium and the two other neighboring phosphorus atoms. Compound **4** was also confirmed by a single crystal X-ray diffraction study and the molecular structure of which is shown in Fig. 2. The metal amine bond distance is Rh–N 2.205(2) Å and the phosphine trans to this hemilabile ligand has a short Rh–P(2) bond length of 2.2356(9) Å. Although the other phosphine atom in dppb shows a slightly elongated Rh–P distance of Rh–P(3) 2.3393(10) Å, the P,N ligand also has a considerably short Rh–P(1) bond at 2.2894(9) Å. Similar bond distances have been observed in related P,N rhodium systems [24–30]. Indeed, the rhodium amine bond distances in an analogous aminophosphinite bis-chelate complex derived from an *N*-substituted ephedrine group, developed by Alper and co-workers [29], were 2.201(3) and 2.182(3) Å, where the amine ligands also adopted a configuration that was *trans* to the softer phosphorous atoms. The relatively compressed P(1)–Rh–P(3) angle of 147.32(3) presumably results from steric crowding arising from the bulky secondary aryl amine group. The arylspiroborate anion in **4** shows no appreciable bonding to the metal center and the B–O lengths, ranging from 1.479(4) to 1.493(4) Å, are typical for those found in related systems [31], yet considerably longer than those in **3**, where the boron atom is three coordinate.

In comparison, reactions of pinacolborane (HBpin, pin = 1,2-$O_2C_2Me_4$) and **L1** at room temperature or at elevated temperatures (THF at reflux), *even in the presence of a rhodium catalyst*, failed to generate any significant amounts of the reduction product **5**, as ascertained by multinuclear NMR spectroscopy. Indeed, we have found that **5** could only be produced using a catalytic amount (5 mol%) of rhodium using a microwave reactor at elevated temperatures and pressures [32].

We then decided to look at addition of boranes to the iminophosphine species **L2** to see what affect increasing the steric bulk on the imine group had on activities and selectivities. Not surprisingly, addition of one equivalent of $H_3B{\cdot}SMe_2$ to **L2** gave the corresponding phosphine–borane adduct **6** in good yield (77%). Although addition of two equivalents of $H_3B{\cdot}SMe_2$ to **L2** gave a number of products, reactions using three equivalents of borane generated **7** cleanly, where the imine has been reduced fully to afford a new RR′NBH_2 species (Scheme 5). The ^{31}P NMR spectra of **7** showed a broad peak at δ 21.2 ppm, while the ^{11}B NMR spectra contained two resonances, one at δ 39 ppm for the new NBH_2 boron the other at δ −37 ppm for the four coordinate adduct. To confirm the formation of **7** in these reactions, a single crystal X-ray diffraction study was preformed and the molecular structure of the resulting study is shown in Fig. 3. The P(1)–B(2) bond of 1.9232(17) Å is similar to that seen in related systems [33,34]. For example, the analogous bond in a related borane adduct of a *P,N*-ferrocenyl iminophosphine species is 1.918(4) Å [34]. The N(1)–B(1) bond distance of 1.380(2) Å is somewhat shorter than that

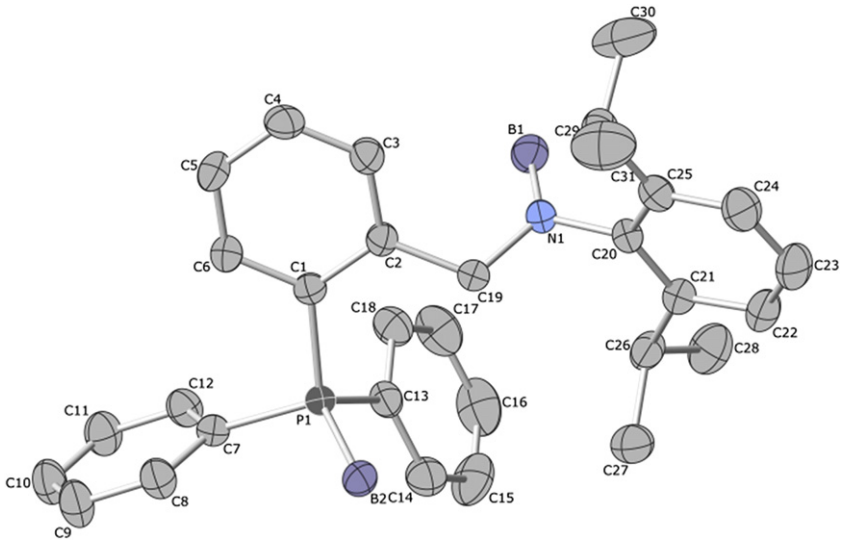
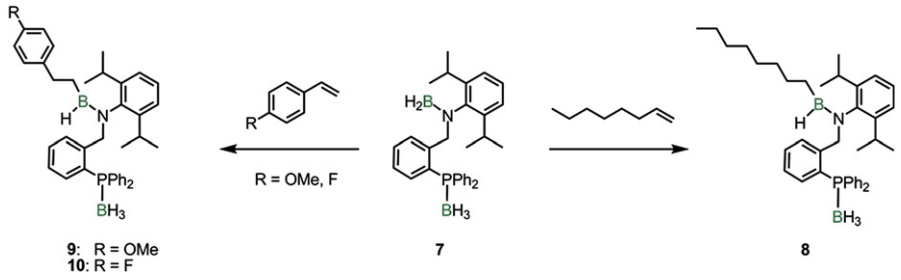


Fig. 3. The molecular structure of **7** with ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond distances (Å): P(1)–B(2) 1.9232(17), N(1)–B(1) 1.380(2), N(1)–C(20) 1.4559(17), N(1)–C(19) 1.4763(18). Selected bond angles (°): C(13)–P(1)–B(2) 114.65(7), C(7)–P(1)–B(2) 111.53(7), C(1)–P(1)–B(2) 113.10(7), B(1)–N(1)–C(20) 120.56(12), B(1)–N(1)–C(19) 125.93(12), C(20)–N(1)–C(19) 113.22(11).



Scheme 6. Addition of borane **7** to 1-octene and vinyl arenes.

observed in C═NR·BH_3 adducts. For comparison, the N—B distance in the borane adduct of 1,4,6-triazabicyclo[3.3.0]oct-4-ene, which retains the imine functionality, is 1.552(2) Å [35,36]. The two nitrogen carbon distances in **7** are similar at N(1)—C(20) 1.4559(17) and N(1)—C(19) 1.4763(18) Å, as expected for the reduced product. What is remarkable about **7** is that we have isolated a novel monosubstituted borane where the steric bulk of the amido group, unlike in the case with **L1**, prevents the B—H bond from reacting further with the bulky imine **L2** and/or **6**.

To examine the potential use of **7** as a hydroborating reagent, we have carried out some initial studies on simple aliphatic and aromatic alkenes. Indeed, we have found that reactions of **7** with 1-octene proceeded slowly (>48 h) at room temperature to give the corresponding reduced organoborane **8** as the major boron-containing species (Scheme 6). Using elevated temperatures greatly reduced reaction times as the addition was completed within 4 h at 80 °C. Borane **7** could also be used effectively in the reduction of vinyl arenes, with the major product being the expected terminal addition products **9** and **10**. Interestingly, reactions also gave minor amounts of the internal addition product where the boron fragment has added to the carbon alpha to the arene ring. The electronic nature of the vinyl arene group did not appear to have a significant effect on hydroboration selectivities. In the case of 4-vinylanisole, 4% of the branched product was produced, where the steric bulk of the borane was presumably insufficient to affect this reaction with complete selectivity. Similar selectivities have been observed with related monoalkyl- [37,38] and arylboranes [39]. Borane **7** was added to two equivalents of vinyl arene to see if the second B—H could be used to reduce another alkene group. Although longer reaction times were required (12 h), compound **7** could indeed be used to reduce two equivalents of alkene.

Addition of alkyl and dialkylboranes, such as thexylborane and 9-BBN, were also investigated but all afforded a complicated mixture of products. Finally, we examined the addition of HBcat and HBpin to the bulkier iminophosphine **L2**. Although addition of HBcat to **L2** proceeded at room temperature to generate some of the corresponding reduced imine product, reactions were complicated by borane degradation and complicated product distributions. The use of metal complexes to catalyze this addition did not significantly improve yields, and in some cases, more of the degradation products were observed [11]. Additions with HBpin were remarkably sluggish, but considerably cleaner, and the reduced amine product **11** could be isolated, albeit in low yields (24%).

4. Conclusions

We have prepared two iminophosphines with different steric requirements and examined the addition of boranes in an effort to reduce the imine C═N bond. Reactions using borane-dimethylsulfide with the smaller imine afforded adducts arising from initial coordination to the phosphorus atom and then the imine nitrogen. Addition of excess borane-dimethylsulfide eventually led to reduction of the imine and generated an active $RR'NBH_2$ unit, which went on to make additional aminophosphine products. Sterically hindered imines are required to stabilize the newly formed $RR'NBH_2$ units. Initial hydroboration with the new borane **7** showed good selectivity for the linear addition products with both 1-octene and vinyl arenes. Reactions of iminophosphines with alkyl and dialkylborane were also complicated by adduct formation, making reduction of the imine increasingly difficult with increased steric bulk of the borane. Addition of dialkoxyboranes, catecholborane and pinacolborane, were promising for the less hindered imine, but harsh reaction conditions and complicated product distributions were observed in reactions with the sterically-hindered imine. Further work in this area is currently underway in an effort to expand the scope of these reductions, the results of which will be published in due course.

Acknowledgments

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Appendix A. Supplementary material

CCDC 905415, 905422 and 905441 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://ccdc.cam.ac.uk/data_request/cif.

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